



# Simplified Two-Time Step Method for Calculating Combustion Rates and Nitrogen Oxide Emissions for Hydrogen/Air and Hydrogen/Oxygen

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## **Abstract**

A simplified single rate expression for hydrogen combustion and nitrogen oxide production was developed. Detailed kinetics are predicted for the chemical kinetic times using the complete chemical mechanism over the entire operating space. These times are then correlated to the reactor conditions using an exponential fit. Simple first order reaction expressions are then used to find the conversion in the reactor. The method uses a two-time step kinetic scheme. The first time averaged step is used at the initial times with smaller water concentrations. This gives the average chemical kinetic time as a function of initial overall fuel air ratio, temperature, and pressure. The second instantaneous step is used at higher water concentrations ( $>1 \times 10^{-20}$  moles/cc) in the mixture which gives the chemical kinetic time as a function of the instantaneous fuel and water mole concentrations, pressure and temperature (T4). The simple correlations are then compared to the turbulent mixing times to determine the limiting properties of the reaction.

The NASA Glenn GLSENS kinetics code calculates the reaction rates and rate constants for each species in a kinetic scheme for finite kinetic rates. These reaction rates are used to calculate the necessary chemical kinetic times. This time is regressed over the complete initial conditions using the Excel regression routine. Chemical kinetic time equations for  $H_2$  and  $NO_x$  are obtained for  $H_2$ /air fuel and for the  $H_2/O_2$ .

A similar correlation is also developed using data from NASA's Chemical Equilibrium Applications (CEA) code to determine the equilibrium temperature (T4) as a function of overall fuel/air ratio, pressure and initial temperature (T3). High values of the regression coefficient  $R^2$  are obtained.

## **Introduction**

Hydrogen is the fuel of the future. Iceland is converting their economy to hydrogen and several countries (United States, Germany, Australia, Mexico, China, Canada, Japan, and Russia) are strongly interested in the technology because of global warming concerns from  $CO_2$  and the unlimited supply of hydrogen from water conversion. It is important to have a simple, quick

method of computing the chemical rates for prediction of times of conversion and for the design of combustors. Accurate chemical kinetic mechanisms exist for hydrogen reaction, but they involve as many as 21 chemical steps with the production of intermediate species like OH, HO<sub>2</sub>, H and O atoms with H<sub>2</sub>O<sub>2</sub> as an intermediary. We have used the H<sub>2</sub> mechanism of S.L. Hwang et al. (ref. 1), as the basis of this report. No changes in the hydrogen mechanism were made in switching from H<sub>2</sub>/Air to H<sub>2</sub>/O<sub>2</sub>. We have taken a forty-two step mechanism for the production of nitrogen oxides from Gri-Mech 2.1 without the carbon reactions, used in reference 2, and correlated the formation rate of nitrogen oxides in the presence of hydrogen by a similar two-time step method. Any detailed mechanism could have been used to compute the chemical kinetic time constants.

Large mechanisms with many intermediate species and very fast radical reactions cause the equations to be stiff (extremely fast compared to the overall rate, requiring a large number of small time steps), making them very difficult to integrate. Calculations for these extensive mechanisms are repetitive and complex. Using the simplified kinetic scheme developed here to calculate the two chemical kinetic times greatly reduces the amount of time required to compare kinetic reaction times with turbulent mixing times and will reduce the time required to obtain a converged solution. The advantage of extracting the chemical kinetic time for only the species of interest from a detailed computation is that we have only the differential equations of interest to solve, resulting in a much smaller set of equations.

The hydrogen reactions are about seven times as fast as hydrocarbon fuels and the reactions require small time steps to integrate accurately. We have used the NASA Glenn GLSENS kinetics code (ref. 3) to integrate the progress of the reaction accurately. The classical methods were used to compute over two thousand cases at constant T and P. Then the results were correlated with a simple two-time step approach to predict the chemical kinetic time constants. The derived method involves only the principal species H<sub>2</sub>, and H<sub>2</sub>O and NO<sub>x</sub> for nitrogen oxides, species which are predicted routinely by computer codes. We do not require tracking the intermediate free radicals, as the kinetic times in step one before the radicals become large are practically constant and in step two are related to the instantaneous H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O concentrations .

We have also curve fitted the equilibrium temperature T<sub>4</sub> using data generated by the NASA Chemical Equilibrium Application code (CEA) to an exponential equation.

The NASA detailed kinetics code (GLSENS) (ref. 3), was used to integrate the system of equations at constant temperature and pressure, at over 2000 initial conditions to derive the rate expressions. We have massively correlated the output from GLSENS, into simple exponential expressions for the chemical kinetic times using the Excel regression routines. It may be reasoned that the presented equations are only as good as the overall mechanism that calculates the data. However, performing the calculations in the conventional manner is also only as good as the mechanism equations and constants that go into them.

The two-time step approach was used successfully by Molnar and Marek in reference 2 for Jet-A and methane. The two-time step approach is used because the free radicals OH, etc., catalyze the reactions and act as important intermediates. The principle reaction for water production is OH through the reaction



We think that the more water that is present in the reactor then the more OH would be present accelerating all of the reactions. So H<sub>2</sub>O can be used as an indicator of the OH present.

The report will present the section Mixing/Kinetics, Model Equations, Equilibrium Fits, Determination of the Chemical Kinetic Time, and the Chemical kinetic time equations for both the H<sub>2</sub>/air and the H<sub>2</sub>/O<sub>2</sub> mixtures. The principal difference in the conditions is in the maximum range of pressures and temperatures considered, see Table Input, and the lack of the diluent nitrogen for the H<sub>2</sub>/O<sub>2</sub> condition. Comparisons of the correlations for different fuels and a comparison of NO<sub>x</sub> production data from reference 2 is given.

## Mixing Times Versus Chemical Kinetics Times

Reaction rates are kinetically limited at low temperatures and mixing limited at very high temperatures. According to the Magnussen model (ref. 4), the fuel oxidation rate will be determined by the maximum of either the chemical kinetic time or the turbulent mixing times of the fuel and air. However, for large numerical solutions it is very tedious to use detailed classical calculations to compare both the kinetic and turbulent mixing times to determine the limits of the reaction. Detailed chemical kinetic schemes are extremely time consuming for two- and three-dimensional computer calculations for combustors.

The Magnussen model (ref. 4) proposes that the maximum of either the turbulent mixing or the chemical kinetic times will be the limiting factor of a chemical reaction. This model could be explored by numerically calculating both times to compare them. However, using detailed mechanisms, this is a long and tedious process. The calculations would be extremely complicated for the detailed chemical kinetic time. By using the equations presented here to determine the chemical kinetic times and using conventional numerical methods to determine mixing times, the Magnussen model can be applied in a much more convenient way.

$$\text{Net rate } \varpi_r = \min\left(\frac{A\varepsilon}{k} y_{fuel}, \frac{A\varepsilon}{k} \frac{y_{oxygen}}{r_f}, \varpi_{kinetic}\right) \quad (2)$$

Where  $\frac{k}{A\varepsilon}$  equals the turbulent mixing time,  $\tau_m$ , with  $k$  being the turbulent kinetic energy,  $\varepsilon$  is the dissipation rate,  $y$  is the mass fraction, and  $r_f$  is the stoichiometric coefficient written on a mass fraction basis. The mixing constant,  $A$ , is usually given as 4.0. The factor  $\frac{y_{fuel}}{\varpi_{kinetic}}$  is the chemical kinetic time  $\tau_c$  computed in this report from the correlations presented.

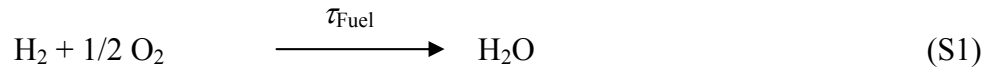
In order to obtain the chemical source term  $\varpi_r$ , a comparison is made of the mixing rate,  $\frac{1}{\tau_m}$  and the chemical kinetic rate  $\frac{1}{\tau_c}$ , and the lowest rate or the longest time is used in the expression (see fig. 1). This may also be represented by the following relationship:

$$\tau = \max(\tau_m, \tau_c) \quad (3)$$

With the approach derived here, a simple direct comparison can be made between the mixing and chemical kinetic times and the minimum rate used for the computation.

## Model Equations

The following equations can be used to model the chemical system.



The following first order reaction was used to represent the rate of fuel burning. We compute the net reaction time so we do not worry about the forward and reverse processes, only the net process. We assume that the fuel goes to zero at the end of the reaction and that the NO<sub>x</sub> increases linearly and it is far from equilibrium. (In this report,  $t$  and  $\tau$  are given in milliseconds, except  $\tau_{\text{NO}_x}$  which is in  $\frac{\text{ms} \cdot \text{cc}}{\text{gmol}}$ , while concentrations are given in gmol/cc):

$$\frac{dH_2}{dt} = -\frac{cH_2}{\tau_{H_2}} \quad (4); \quad \text{SO} \quad \tau_{H_2} = -\frac{cH_2}{\sum \left( \frac{dH_2}{dt} \right)}$$

$$\text{OR if } \tau_{H_2} \text{ is constant:} \quad H_2 = H_{2_o} e^{\left( \frac{-t}{\tau_{H_2}} \right)}$$

For a constant  $\tau_{H_2}$ , the fuel concentration is then represented by a simple exponential decay expression, where  $H_{2_o}$  is the initial fuel concentration.

The nitrogen oxide formation rate, a species important for combustor emissions, was modeled as a simple zero order expression.

$$\frac{d\text{NO}_x}{dt} = \frac{1}{\tau_{\text{NO}_x}^*} \quad (5) \quad \text{OR if } \tau_{\text{NO}_x} \text{ is constant} \quad \text{NO}_x = \frac{t}{\tau_{\text{NO}_x}^*} \quad (6)$$

$$\tau_{\text{NO}_x}^* \text{ has units of } \frac{\text{ms} \cdot \text{cc}}{\text{gmol}}$$



## Determination of Chemical Kinetic Time

Using equations (4) and (5) above, the dependent chemical kinetic times ( $\tau_{\text{Fuel}}$ ,  $\tau_{\text{NOx}}$ ) can be easily computed and correlated against several independent variables using the Excel regression routines. The integration was performed for 1256 cases for the H<sub>2</sub>/air and 2808 cases for the H<sub>2</sub>O<sub>2</sub> conditions shown below:

### TABLE-INPUT: INITIAL CONDITIONS FOR COMPUTATIONS

#### H2/Air Inlet Conditions:

##### Equilibrium H2/Air

H2(g) = 294.44 K

Air = 294.44 K, 589.89 K, 922.22 K, 1255.55 K

Pressure = 1, 20, 40, 60 atm

Lean equivalence ratios = 0.2 to 1.0 increments of 0.1

Rich equivalence ratios = 1.05, 1.1 to 2.0 increments of 0.1.

##### Initial conditions for chemical kinetic times for H2/Air

Temperature = 1000., 1500., 2000., 2500. K

Pressure = 1, 10, 20, 30, 40 atm

Lean equivalence ratios = 0.3 to 1.0 increments of 0.1

Rich equivalence ratios = 1.05, 1.1 to 2.0 increments of 0.1

#### H2/O2 Inlet Conditions:

##### Equilibrium H2/O2

H2(g) = 30., 100., 200., to 500. K increments of 100. K

O2(g) = 50., 100., 150. K

Pressure = 1, 50, 100, 200, 300, 400 atm\*

Lean equivalence ratios = 0.1 to 1.0 increments of 0.1

Rich equivalence ratios = 1.05, 1.1, 1.2 to 3.0 increments of 0.2

##### Initial conditions for chemical kinetic times for H2/O2

Temperature = 1000., to 4000., increments of 500, then 5000. K

Pressure = 0.5, 1., 10., 50., 100., 200., 300., 400. atm

Lean equivalence ratio = 0.1 to 1.0 increments of 0.1

Rich equivalence ratio = 1.05, 1.1, 1.2 to 3.0 increments of 0.2

\* These conditions are for advanced rocket combustors (ref. 5).

Time steps for step 1 was integrated to a water concentration of  $1 \times 10^{-20}$  and time step 2, the instantaneous chemical kinetic times were computed to 0.1 ms. The output for time step 2 is every integration step after the water concentration was above  $1 \times 10^{-20}$ , with up to 20 points tabulated per case. The total number of points could exceed 20 000.

Microsoft Excel (Microsoft Corporation, Redmond, WA) can handle up to 65 000 points.

The supplied kinetic mechanism was used for the full range of conditions without modification. Even though the mechanism was tested to a temperature of 3 000 K and 4 atm, we felt that the mechanism would extrapolate and give reasonable results for design since nothing else was available at the high temperature and high pressure conditions. The differences between

the H<sub>2</sub>/air and the H<sub>2</sub>/O<sub>2</sub> is the absence of nitrogen in the H<sub>2</sub>/O<sub>2</sub> set, and in H<sub>2</sub>/O<sub>2</sub> the maximum temperatures were twice that of H<sub>2</sub>/air and the maximum pressures were an order of magnitude higher. We computed and correlated the chemical kinetic times over the full range of conditions.

For all time steps, calculations were performed isothermally using GLSENS for each condition over a time of 0 to 3 ms. By computing the progress isothermally, the chemical rate constants were nearly fixed and averaged over the total time for step one and instantaneous chemical kinetic times were computed for step two:

$$\frac{1}{\tau_{average}} = \frac{1}{t_{total}} \int \frac{dt}{\tau_{instantaneous}} \quad (7)$$

The chemical kinetic time was determined as a unique value of temperature, pressure, and instantaneous mole fractions of fuel and water. GLSENS computes the cumulative rate of reaction for each species from all equations in the mechanism, so it is a simple matter to then compute the chemical kinetic time for each species.

$$\left. \frac{dcH_2}{dt} \right|_{total} = \sum \left. \frac{dcH_2}{dt} \right|_i \quad (8)$$

For the fuel equation (4) the chemical kinetic time is given as

$$\tau_{H_2} = - \frac{cH_2}{\sum \left( \frac{dH_2}{dt} \right)} \quad (9)$$

This simple calculation was done using additional steps in Subroutine Out2 in the GLSENS code (see appendix B). Values for the chemical kinetic time were calculated for each concentration at each output time and each set of conditions. For time step 1, the trapezoidal rule (using  $1/\tau$ ) was used to average the chemical kinetic time to calculate the best value for each set of conditions and the final numbers regressed over the complete set of cases to obtain the final correlation.

A correlation could then be developed that determines the chemical kinetic time as a function of the initial overall cell fuel/air ratio, pressure and temperature. The data was correlated using the same method as previously mentioned for the equilibrium equations. Two correlations for each step for each of the two species, one for the lean side and one for the rich side, were obtained. This results in a total of 4 H<sub>2</sub> correlations for H<sub>2</sub>/air and 2 H<sub>2</sub>/O<sub>2</sub> correlations. As OH is formed, the reaction rates get faster and the chemical kinetic time gets smaller. The chemical kinetic time was correlated using two different steps to increase the accuracy of the calculation. Step one is an average chemical kinetic time taken over 3.0 ms. Step two is an instantaneous value that depends on the instantaneous amounts of fuel, water, and oxygen. Since we were not tracking the radical concentrations, we were using H<sub>2</sub>O to indicate the state of the radical species. In other words for the reactions





The radicals could be correlated with  $\text{H}_2\text{O}$  because of the first reaction.

The user would switch from step one to step two when the molar concentration of water is greater than  $1 \times 10^{-20}$  moles/cc. This value was chosen arbitrarily as a simple switch to transition when the rates accelerated. Step two can not be used with small concentrations of water because if the value of the water concentration was zero, the entire correlation time would go to zero and the rate would be computed as infinity.

## H<sub>2</sub> Kinetic Scheme For Step 1 (Average) and Step 2 (Instantaneous) Methods

The following is GLSENS input for the 21 step, 8 species mechanism from reference 1 and the 42 step NO equations from GRI-Mech 2.1, without the carbon reactions from reference 2 that were used for the  $\text{H}_2$  calculations for a total of 63 mechanism steps and 15 species.

TAPE

NEW H2 MECHANISM OF S.M.Hwang, et. al. (reference 1)

```
&RTYPE GLOBAL=.TRUE.,GRONLY=.FALSE. &END
  H      O2      =      OH      O      6.73E+15      -0.499      26671.6
  O      H2      =      OH      H      5.06E+04      2.67      6289.2
  OH     H2      =      H2O     H      2.16E+08      1.510     3430.0
  O      H2O     =      2.OO    H      4.51E+04      2.7      14551.4
  O      O       =      O2      M      1.00E+17      -1.      0.0
  THIRDBODY
H2O     18.5     H2      2.9      O2      1.2      END
  H      H       =      H2      M      6.4E+17      -1.      0.0
  THIRDBODY
H2O     12.0     H2      4.0      H      26.      END
  H      O       =      OH      M      6.2E+16      -0.6     0.0
  THIRDBODY
H2O     5.       END
  H      OH      =      H2O     M      8.4E+21      -2.      0.0
  THIRDBODY
H2O     16.25    H2      2.5      END
  H      O2      =      HO2     M      5.55E+18      -1.15    0.0
  THIRDBODY
H2O     21.3     H2      3.33     O2      1.33     END
  HO2    H       =      OH      OH      8.4E+13      0.0      635.0
  HO2    H       =      H2      O2      2.5E+13      0.0      693.1
  HO2    H       =      H2O     O      5.0E+12      0.0      1410.1
  HO2    O       =      O2      OH      2.0E+13      0.       0.
  HO2    OH      =      H2O     O2      2.0E+13      0.       0.
  HO2    HO2     =      H2O2    O2      1.3E+11      0.      -1630.0
  HO2    HO2     =      H2O2    O2      4.2E+14      0.      11999.5
  M      H2O2    =      2.OOH   M      1.2E+17      0.      45506.7
  THIRDBODY
H2O     6.0      O2      0.78     END
  H2O2   H       =      HO2     H2      1.7E+12      0.      3776.3
```

H2O2	H	=	H2O	OH	1.0E+13	0.	3585.1
H2O2	O	=	HO2	OH	2.8E+13	0.	6405.4
H2O2	OH	=	H2O	HO2	1.0E+12	0.	0.
H2O2	OH	=	H2O	HO2	5.75E+12	0.	9559.8
N	NO	=	N2	O	3.500E+13	.000	330.00
N	O2	=	NO	O	2.650E+12	.000	6400.00
N	OH	=	NO	H	7.333E+13	.000	1120.00
N2O	O	=	N2	O2	1.400E+12	.000	10810.00
N2O	O	=	2.0	NO	2.900E+13	.000	23150.00
N2O	H	=	N2	OH	4.400E+14	.000	18880.00
N2O	OH	=	N2	HO2	2.000E+12	.000	21060.00
M	N2O	=	N2	O	1.300E+11	.000	59620.00
THIRDBODY							
H2	2.00		H2O	6.00	N2	0.625	END
HO2	NO	=	NO2	OH	2.110E+12	.000	-480.00
NO	O	=	NO2	M	1.060E+20	-1.410	.00
THIRDBODY							
H2	2.00		H2O	6.00	N2	0.625	END
NO2	O	=	NO	O2	3.900E+12	.000	-240.00
NO2	H	=	NO	OH	1.320E+14	.000	360.00
NH	O	=	NO	H	5.000E+13	.000	.00
NH	H	=	N	H2	3.200E+13	.000	330.00
NH	OH	=	HNO	H	2.000E+13	.000	.00
NH	OH	=	N	H2O	2.000E+09	1.200	.00
NH	O2	=	HNO	O	4.610E+05	2.000	6500.00
NH	O2	=	NO	OH	1.280E+06	1.500	100.00
NH	N	=	N2	H	1.500E+13	.000	.00
NH	H2O	=	HNO	H2	2.000E+13	.000	13850.00
NH	NO	=	N2	OH	2.160E+13	-.230	.00
NH	NO	=	N2O	H	4.160E+14	-.450	.00
NH2	O	=	OH	NH	7.000E+12	.000	.00
NH2	O	=	H	HNO	4.600E+13	.000	.00
NH2	H	=	NH	H2	4.000E+13	.000	3650.00
NH2	OH	=	NH	H2O	9.000E+07	1.500	-460.00
H	NO	=	HNO	M	8.950E+19	-1.320	740.00
THIRDBODY							
H2	2.00		H2O	6.00	N2	0.7	END
HNO	O	=	NO	OH	2.500E+13	.000	.00
HNO	H	=	H2	NO	4.500E+11	.720	660.00
HNO	OH	=	NO	H2O	1.300E+07	1.900	-950.00
HNO	O2	=	HO2	NO	1.000E+13	.000	13000.00
NH3	H	=	NH2	H2	5.400E+05	2.400	9915.00
NH3	OH	=	NH2	H2O	5.000E+07	1.600	955.00
NH3	O	=	NH2	OH	9.400E+06	1.940	6460.00
NH	+ NO	=	N2	+ OH	2.00E+15	-.8	0.
H	O2		H2O	= HO2	H2O		
1.	1.	1.			9.380E+18	-.760	.00
H	O2		N2	= HO2	N2		
1.	1.	1.			3.750E+20	-1.720	.00

The hydrogen mechanism was not changed for the H<sub>2</sub>/O<sub>2</sub> calculation. Note, some reactions are bimolecular and some are trimolecular expressions so the kinetics code GLSENS was used instead of LSENS. However, the GLSENS code follows the method of LSENS developed by Radhakrishnan (ref. 6).

## H<sub>2</sub>/Air Equilibrium

Equilibrium correlations were generated by using Microsoft Excel to perform a multivariate linear regression on the large data set generated by the CEA program of reference 7. (The detailed procedure describing the regression used for both equilibrium and finite rate chemical times can be found in appendix A). CEA has a plot option for direct tabulation of the output data, for 'f/a, P, T4 H<sub>2</sub>O, NO'. Although the equilibrium correlations were not usually used in the calculation of the chemical kinetic times, we feel that these equations could still be very useful for other calculations of T4 in well stirred reactors or plug flow calculations. Table 1 shows the H<sub>2</sub> equilibrium correlations for T4, and NO<sub>x</sub> for both the lean and rich cases. The exponential function did not correlate the complete data over the total equivalence ratio from 0.2 to 2.0, because of the peak in the values at the stoichiometric conditions. We chose to correlate the values from lean ( $\phi_o = 0.2$  to 1.) and then rich from ( $\phi_o > 1.0$  to 2.0). A similar approach was used for the chemical kinetic times. Figure 2 is a parity plot showing the strength of the lean T4-H<sub>2</sub>/air equilibrium correlation. This plot shows a minimal amount of scatter, mostly at an equivalence ratio of 1.0, indicating a good correlation ( $R^2$  values greater than 0.9).  $R^2$  is based on the logarithm of the variables (see appendix A). Using the logarithms, the errors are relative errors so errors at the small times are weighted equally to errors at large times. An  $R^2$  of one is a perfect correlation. Although the scatter looks large for some parity plots, the mean error looks good over the 1000 points. The correlation is very good over a variable range of seven orders of magnitude. Note that the units of NO<sub>x,eq</sub> are mole fraction. This parity plot is typical of all the variables because of the good  $R^2$  values obtained. The lean T4 and NO<sub>x</sub> equations were correlated over the complete temperature, pressure and phi range of independent variables in the Table Input.

$$T4 = A(P)^a (T3)^b (\phi_o)^c \quad (12)$$

$$NO_{x,eq}(\text{mole fraction}) = A(P)^a (\phi_o)^b \exp\left[\frac{E}{T4}\right] \quad (13)$$

Although these equations seem complex, they are simple to program and use. Calculations can even be done on a hand calculator.

**Table 1.—EQUILIBRIUM Lean and Rich H<sub>2</sub>/Air Correlations**

<b>T4 eq Equations</b>					
	A	Pressure	T3	$\phi_o$	Rsquared
Lean T4	476.9	0.00419	0.261	0.432	0.936
Rich T4	1217.0	0.00727	0.120	-0.243	0.962
<b>NO<sub>x</sub> eq Equations</b>					
	A	Pressure	$\phi_o$	1/T4	Rsquared
Lean NO <sub>x</sub> eq	0.616	-0.0153	-0.810	-11382.3	0.977
Rich NO <sub>x</sub> eq	21168.	-0.475	-4.080	-39583.4	0.991

(14)

(15)

(16)

(17)

## Chemical Kinetic Times for H<sub>2</sub>/Air

### Step One Equations for H<sub>2</sub>/Air

The following form of equation was used for the H<sub>2</sub> and NO<sub>x</sub> step one correlations:

$$\tau = A(P)^a (\phi_o)^b \exp \frac{E}{T} \quad (18)$$

where  $\tau$  is the chemical kinetic time in milliseconds,  $P$  is pressure in atm,  $f/a$  is the initial or overall mass fuel air ratio as in reference 2, and  $T$  is the temperature in Kelvin. The correlation is switched to Step Two when the water molar concentration is greater than  $1 \times 10^{-20}$  moles/cc, see the next section.

The coefficients for each of the parameters in the correlations may be found in Table 3. R-square values have been included to demonstrate the strength of the correlation. R-squared is a measure of the error in the model; an R-squared value of one is ideal.

Since the radical and intermediate species concentrations are very small, the initial or overall fuel air ratio can be determined from the molar concentration of  $cH_2$ ,  $cH_2O$  and  $cN_2$  moles/cc as follows:

$$f / a = (cH_2 + cH_2O) * 2 * \frac{0.79}{29 * cN_2} ; \text{ and } \phi_o = f/a / 0.0292 \quad (19)$$

**Table 2.—Step One H<sub>2</sub>/Air Chemical Kinetic Time Correlations**

		<b>A</b>	<b>a</b>	<b>E</b>	<b>b</b>	<b>Rsquared</b>	
H <sub>2</sub> /Air	Lean	4.671E-5	-1.036	25068.	0.539	0.994	(20)
H <sub>2</sub> /Air	Rich	3.223E-5	-1.032	24223.	1.832	0.951	(21)
No <sub>x</sub>	Lean	2.36E5	-1.670	45085.	0.472	0.647	(22)
No <sub>x</sub>	Rich	1.831	1.484	49802.	-5.91	0.397	(23)

All of the results presented here are correlated over the complete conditions listed in the Table Input, initial  $f/a$ , temperature, and pressure of the reactor. Parity plots for the lean step one correlations have been created and may be found in figures 4 to 5. The x-axis contains values for the chemical kinetic time generated by the full mechanism GLSENS at each condition. The y-axis contains values calculated using the chemical kinetic time correlations above at the same set of conditions. This parity plot demonstrates how close the calculated value is to the full mechanism value and is a good measurement of the strength of the correlations. The rich parity plots are similar to the lean plots shown here and are not repeated.

### Step Two Equations for H<sub>2</sub>/Air

The following form of equation was used for both the Tau H<sub>2</sub> step two fuel and NO<sub>x</sub> correlations except for different constants. This form of the equation produced the best fit:

$$\tau = A(P)^a (cH_2)^b (cH_2O)^c (\phi_o)^d \exp \frac{E}{T} \quad (24)$$

where  $P$  is pressure in atm,  $cH_2$  is the instantaneous molar concentration of  $cH_2$  and  $cH_2O$  is the instantaneous water concentration. We have preceded the symbol with a “c” to indicate molar concentration moles/cc was used and a “y” for mole fraction. Molar concentration is usually a primary variable of combustor computer codes.  $T$  is the mixture temperature in Kelvin. We have correlated to only the major species hoping that  $cH_2O$  will track the minor species (OH, H, O, etc.) to allow good overall correlation and easy to use equations.

The coefficients for each parameter are given in table 3. Parity plots for the step two lean  $H_2$  correlations can be found in figures 6 and 7. These figures show considerable scatter for the fuel and small amount for  $NO_x$ . The hydrogen mechanism used is difficult to model with the current equations as indicated by the scatter. However the correlations are good for design and large numerical calculations where kinetics are important.

**Table 3.—Constants in Equation (24) Step Two  $H_2$ /Air Kinetic Time Correlations**

		A	a	E	b	c	d	Rsquared	
$H_2$ /Air	Lean	1.89E-14	0.605	18497.	-0.803	-0.630	2.41	0.604	(25)
$H_2$ /Air	Rich	5.91E-34	3.80	26071.	-3.80	-0.511	8.24	0.431	(26)
$NO_x$	Lean	1.45E-10	-0.0092	48747.	-0.479	01.042	2.052	0.967	(27)
$NO_x$	Rich	1.26E-19	1.566	49662.	-2.01	-0.932	5.99	0.869	(28)

## $H_2/O_2$ Equilibrium Correlations

The  $H_2/O_2$  presentation closely follows the  $H_2$ /air presentation. The lean and rich  $H_2/O_2$  equilibrium correlations can be found in table 4, respectively. A parity plot for the lean  $H_2/O_2$  T4 equilibrium correlation can be found in figure 8. T3 is the initial temperature for  $H_2$  and  $O_2$  whose state were taken to be gaseous. These temperatures for rockets is considerably lower than for  $H_2$ /air combustors.

$$T_4 = A(P)^a (\phi_o)^b (T_{3H_2})^c (T_{3O_2})^d \quad (29)$$

**Table 4.—EQUILIBRIUM  $H_2/O_2$  Correlations**

	A	a	b	c	d	Rsquared
Lean T4	1.46E-109	0.0248	0.393	8.96	58.4	0.91
Rich T4	0.96	0.021	-0.427	0.395	1.752	0.92

Where the equivalence ratio  $\phi$  for  $H_2/O_2$  is given by:

$$\phi_o = \frac{cH_2^o}{2 * cO_2^o} \quad (30)$$

## Chemical Kinetic Times For H<sub>2</sub>/O<sub>2</sub>

### Step One Equations for H<sub>2</sub>/O<sub>2</sub>

The lean and rich step one H<sub>2</sub>/O<sub>2</sub> chemical kinetic time correlations are of the following form:

$$\tau = A(P)^a (\phi_o)^b \exp\left[\frac{D}{T}\right] \quad (31)$$

where P is pressure in atm,  $\phi$  is the initial or overall equivalence ratio and T is the temperature in Kelvin.

The initial or overall fuel oxygen ratio can be determined from either the initial or the mixture molar concentrations of cH<sub>2</sub>, cH<sub>2</sub>O and cO<sub>2</sub> moles/cc. Assuming that the radical and intermediate concentrations are small, the initial cH<sub>2</sub> concentration is:

$$cH_2^o = cH_2 + cH_2O \quad (32)$$

A summary of these correlations can be found in table 5. Parity plots for the lean step one H<sub>2</sub>/O<sub>2</sub> correlations can be found in figure 9. These parity plots show minimal scatter, which is consistent with the high R-squared values of the lean correlations.

**Table 5.—Step One H<sub>2</sub>/O<sub>2</sub> Chemical Kinetic Time Correlations**

	A	a	D	b	Rsquared
Lean	2.632E-5	-1.005	24244.	0.771	0.975
Rich	1.397E-5	-1.024	24799.	1.141	0.971

(33)

(34)

## Two Step H<sub>2</sub>/O<sub>2</sub> Chemical Kinetic Times

### Step Two Equations for H<sub>2</sub>/O<sub>2</sub>

The following form of equation was used for all lean and rich H<sub>2</sub>/O<sub>2</sub> step two correlations:

$$\tau = A(P)^a (cfuel)^b (ch_2O)^c (\phi_o)^d \exp\left[\frac{E}{T}\right] \quad (35)$$

Table 6 provides a summary of these correlations, and lean parity plots can be found in figure 10.



**Table 6.—Step Two H<sub>2</sub>/O<sub>2</sub> Chemical Kinetic Time Correlations**

	<b>A</b>	<b>a</b>	<b>E</b>	<b>b</b>	<b>c</b>	<b>d</b>	<b>Rsquared</b>
Lean	1.114E-13	0.645	8028	-1.000	-0.664	1.785	0.358
Rich	2.196E-24	2.544	25388	-3.079	0.035	4.24	0.315

(36)

(37)

### **Comparison of Kinetic Times for Hydrogen and NO<sub>x</sub> for Multiple Fuels**

The multiple fuel kinetic times at 10 atm and 2000 K are shown for step one in figure 11 and for step two in figure 12. The Jet-A and methane predictions were obtained from reference 2. For step one the kinetic times are one millisecond for lean mixtures except for Jet-A which was 10 μs. The Jet-A mechanism consisted of a irreversible breakup to CH and C<sub>2</sub>H<sub>2</sub> followed by oxidation of the products. These times are the average startup times computed when the water concentration is less than 1×10<sup>-20</sup>. Without nitrogen, the rate for H<sub>2</sub>/O<sub>2</sub> is faster than H<sub>2</sub>/air. Step two, figure 12, is computed with an inefficiency of 0.5, or 50 percent reacted. After the radicals form, the rates are much faster being 1μs for H<sub>2</sub>/O<sub>2</sub> at an equivalence ratio of 0.6. The smaller the chemical kinetic time, the faster is the reaction. The chemical kinetic times for NO<sub>x</sub> step one and two (INEFF = 0.5 see below) are shown in figure 13. The NO<sub>x</sub> production rate with hydrogen was two orders of magnitude slower than for Jet-A or methane.

### **Computation of the Fuel and Water Concentrations for Step Two**

In order to use the step two instantaneous correlations, one needs to know the instantaneous fuel and water concentrations and the temperature and pressure. Remember, these correlations were based on the model concentrations for H<sub>2</sub> and H<sub>2</sub>O. The concentrations can be easily computed from the inefficiency, INEFF, where

$$INEFF = \frac{cH_2}{cH_2^o} \quad (38)$$

If  $cH_2^o$ , the initial hydrogen concentration is unknown it equals:

$$cH_2^o = cH_2 + cH_2O \quad (39)$$

or can be computed from the initial f/a or initial equivalence ratio  $\phi_o$  from:

$$cH_2^o = \frac{f/a * 29/2 * \rho}{(1 + f/a * 29/2)} \quad (40) \quad \text{where } f/a = \phi_o * 0.0292$$

$$\rho = \frac{P}{82.056 * T} \text{ moles/cc} \quad (41)$$

Then, from equations (38) and (39), the concentrations are:

$$cH_2 = cH_2^o * (INEFF) \quad (42)$$

$$cH_2O = cH_2^o - cH_2 = cH_2^o * (1 - INEFF) \quad (43)$$

$$cO_2 = cO_2^o - \frac{1}{2} cH_2O \quad (44)$$

$$cN_2^o = \frac{0.79}{0.21} * cO_2^o \quad (45)$$

The initial equivalence ratio  $\phi_o$  for either  $H_2$ /air or  $H_2$ / $O_2$  is given by:

$$\phi_o = \frac{1}{2} * \frac{cH_2^o}{cO_2^o} \quad (46)$$

These values were substituted into step two kinetic time constants equations at 10 atm 2000 K and an INEFF = 0.5 and plotted in figure 13.

The step two chemical kinetic times can be computed from equations (24) and (35) above for a Tau given by the values in tables 3 and 6 at conditions of P = 10 atm, T = 2000 K, and INEFF = 0.5.

### Comparison of the Model With the Full Mechanism Kinetics

The predictions of the full mechanism ( $H_2$ ,  $H_2O$ ,  $OH$ , and  $H_2O$ ) are plotted in figures 14 and 15, and then our model predictions are superimposed on the calculations. The model predictions are slower than the full mechanism predictions. We have not included the intermediate species in our predictions, but we correlate the chemical kinetic times to the overall species concentrations. The inefficiency from the above equation (38) is integrated using the chemical kinetic time, Tau ( $\tau$ ).

$$INEFF = \frac{cH_2}{cH_2^o} = \exp\left(\int -\frac{dt}{\tau_{H_2}}\right) \quad (47)$$

where  $\tau_{H_2} = \tau_{H_2}$  at the start or

$$\tau_{H_2} = \tau_{H_2O} \text{ when } cH_2O > 1 \times 10^{-20}.$$

This single equation was integrated by backward differencing for a time step of  $1 \times 10^{-6}$  ms. Even at the first time step of  $1 \times 10^{-6}$  sec, the water concentration is at  $1 \times 10^{-13}$ , so only step two was used in these calculations. One could have used a Runge Kutta scheme, but this simple example could be quickly implemented on an Microsoft Excel spreadsheet. The chemical kinetic

time for this condition is about 10  $\mu$ s so the integration requires only about 3000 steps. The agreement is fair for the three species of interest. As expected the OH, H, and O increases at almost the same rate as the H<sub>2</sub>O, so it is a good indicator of the reaction rate.

### Computation of NO<sub>x</sub> PPM

One can use the correlations for computing premixed NO<sub>x</sub> levels for well mixed combustors. The NO<sub>x</sub> in parts per million (ppm) or the emission index (EI) can be computed using equation (6).

$$NO_x \left( \frac{\text{mole}}{\text{cc}} \right) = \frac{t}{\tau_{NO_x}} \quad (6)$$

The chemical kinetic time  $\tau_{NO_x}$  ms cc/mole was integrated for a stoichiometric equivalence ratio in figure 14. A NO<sub>x</sub> concentration of  $1 \times 10^{-9}$  moles/cc is predicted.

The concentration in ppm is calculated as follows:

$$NO_x(\text{ppm}) = \frac{NO_x \left( \frac{\text{moles}}{\text{cc}} \right)}{\rho \left( \frac{\text{moles}}{\text{cc}} \right)} \times 10^6 \quad \text{where} \quad \rho = \frac{P}{RT} = 6.09 \times 10^{-5} \quad (48)$$

The NO<sub>x</sub> concentration in ppm is then 16.42 for one millisecond residence time.

This result is consistent with the data.

### Auto Ignition Times for H<sub>2</sub>/Air

Hydrogen reacts explosively at low temperatures and pressures as shown by the dashed line in figure 16. Mixtures to the right of the curve explode (produce a rapid pressure rise for a constant volume reactor), while mixtures to the left are stable. This was computed by A.K. Oppenheim (ref. 8) using a full mechanism similar to the one used in this report with a one second reaction time.

Auto ignition times using the simple model and a given formula were calculated and compared for the H<sub>2</sub>/air system. The auto ignition time for the simple model is based on the recommendation of reference 9, where the time required for ignition is for 5 percent of the fuel to react.

$$Fuel = F_o e^{-t/\tau} \quad (49)$$

$$\text{If } \frac{Fuel}{F_o} = 0.95 \quad \text{then} \quad \frac{t}{\tau} = 0.0513 \quad \text{and} \quad t_{auto\ ignition} = 0.0513 * \tau_{Fuel} . \quad (50)$$

Note that  $\tau_{fuel}$  decreases as f/a decreases. We used an equivalence ratio of 0.2 (fastest rate from figure 11) with the lean equation.

We limited our correlations to pressures above 0.5 atm. The model above 0.5 atm fits the data well, but it will not capture the “S” shape of the classical data. At low pressures and temperatures, our model would overpredict the stability of the mixture.

The auto ignition delay time was also compared to the correlations of reference 7, shown in figure 17. The formula for calculating the auto ignition time for H<sub>2</sub> (ref. 7) is given by:

$$\tau P(\text{milliseconds} \cdot \text{atm}) = 8.E^{-6} \exp\left[\frac{9600}{T}\right] \quad (51)$$

Figure 17 shows a plot of the auto ignition time versus temperatures that the auto ignition time given by the simple model compares well with the data in reference 8 for  $\tau_2$  and INEFF = 0.95 at the higher temperature. These correlations had a larger activation energy than the expressions of reference 8.

## Conclusions

A simplified kinetic correlation scheme for H<sub>2</sub>/air and H<sub>2</sub>/O<sub>2</sub> fuels resulted in a two-time step correlation that calculates chemical kinetic times for fuel and NO<sub>x</sub>. These models are simple enough to use in spreadsheet calculations and they represent the data well. These chemical kinetic time equations can then be used in a numerical combustor code to compare the chemical kinetic time with the turbulent mixing time at every grid point and for every iteration step. Strong step one ( $R^2 > 0.9$ ) and mild step two ( $R^2 \sim 0.4$ ) H<sub>2</sub> correlations were developed ( $R^2 > 0.9$ ) for all relations, both the H<sub>2</sub>/air and H<sub>2</sub>/O<sub>2</sub> correlations. However, because we are trying to correlate so many values over a wide range of conditions, scatter error exists. These model equations are believed to be extremely useful in the comparison of kinetic reaction and turbulent mixing times and in the computation of kinetic rate results. In our model we have only two equations and four major species, therefore the step size can be large and the rates are no longer coupled. This should be very fast.

## Appendix A

### Multiple Linear Regression With Microsoft Excel

#### Performing Multiple Linear Regression on a Logarithmic Equation

This regression technique may be used to develop a correlation between a dependent variable and one or more independent variables. First the equation to be used must be linearized. An example of an exponential equation used here is shown below.

$$A = BC^c D^d \exp\left(\frac{e}{T}\right) \quad (\text{Non-linear form}) \quad (\text{A1})$$

$$\ln(A) = \ln(B) + c \ln(C) + d \ln(D) + \frac{e}{T} \quad (\text{Linear form}) \quad (\text{A2})$$

Columns of data containing the independent variables (natural log of C, natural log of D, 1/T,) and the dependent variable (natural log of A) were contained in an Excel spreadsheet. (It is easiest to have the independent variables adjacent to each other, followed by the dependent variable.)

The multiple variable regression analysis is located in the Data Analysis Toolpak. The Data Analysis Toolpak must be added into the spreadsheet if it is not already running in Excel. In order to add it, select the 'Add ins' button from the Tools menu. Click on the Analysis Toolpak option and click OK to accept this choice. Then choose 'Data Analysis' from the Tools menu and double click on 'regression'. Click on the 'Input Y Range' box and highlight the column that contains the logarithm of the dependent variable and press return. Click on the 'Input X Range' box and highlight the columns containing all of the independent variables. (In this case  $\ln(C)$ ,  $\ln(D)$  and  $1/T$ ). Press OK to begin the regression. The regression data will be contained in a new worksheet. The variable labeled 'intercept' will be equal to the natural log of coefficient B. The remaining coefficients (c,d, and e) will be given as X Variable 1,X Variable 2 and X Variable 3 respectively. This process is quick and accurate for Excel 2002 and was used for all equations given in this report. Excel has to capability to handle one dependent variable and multiple independent variables. As many as 14,000 points were used in the regressions. Excel can regress up to 65000 points with one dependent variable and 8 independent variables.



## Appendix B

### Modifications to GLSENS for Obtaining Output for the CH<sub>4</sub> Computations

```
C   ALREADY DONE IN DIFFUN
C MODIFICATIONS TO MAIN
COMMON/marek/foa,atauf,atauco,atauno,nc,eratio,edd,timi,nco
C READ AND CONVERT INPUT, PERFORM PRE-KINETIC CALCULATIONS
RXORDR=.TRUE.
write(16,8)
8 format(' fuel, nc, lnP,1/T,ln phi, ln(atau f),atauf,millisecond')
write(18,11)
11 format(' nox, nc, lnP,1/T,ln phi ln(atau f),atauf,millisecond')
icount=0
CALL KINP
5 continue
fo=0.
IF (NEXT) GO TO 55
65 TIME1 = SECCPU(0.0)
IF (WSFLOW) WELSTR = .TRUE.
C AFTER COMPLETION OF EACH TEST CASE, TABULATE THE AVERAGE CHEMICAL
KINETIC TIMES
pln=sngl(dlog(p))
TLN=sngl(1.d0/T)
t1000=log(1000./sngl(T))
fo=0.
phi=foa/0.0292
if(foa.gt.0.)FO=log(phi)
AF=0.
ACO=0.
ANO=0.
if(atauf.gt.0.)AF=log(atauf)
if(atauno.gt.0.)ANO=log(ATAUNO)
icount=icount+1
write(0,31)icount,nc,nco,P,T,phi,timi
C WRITE(14,7)nc,PLN,TLN,FO,AF,ACO,ANO,timi
WRITE(14,31)icount,nc,nco,P,T,phi,timi
31 format(i7,2i10,f10.2,f10.0,f10.3,1p,1e13.4)
7 format(i10,1p,9e13.4)
write(16,7)nco,pln,tln,fo,af,atauf,timi
write(18,7)nco,pln,tln,fo,ano,atauno,timi
atauf=0.
nco=0
nc=0
atauno=0.
CALL RINP
GO TO 5

C MODIFICATIONS TO OUT2 OF LSENS COMPUTE STEP ONE AND STEP TWO FOR EACH
PRINT STATION

C h2lab.f 2/16/2005
C COMPUTE MOLAR CONCENTRATIONS
C ALREADY DONE IN DIFFUN
420 foa=eratio*0.0292
```

```

    phi=eratio
    philn=log(phi)
    tn=timil
    trr=sngl(T)
C   write(6,1605)time
1605 format(' time ',e14.4)
418 if(nc.gt.0)goto 427
    write(10,1)
    1 format(' TITLE= P atm T K f/a coc h2 nox time')
    write(26,444)dsprnm(5),dsprnm(2),dsprnm(1),dsprnm(4),dsprnm(3),dsprnm(6)
    1,dsprnm(10)
444 format(' timil ',1p,13(3x,a8,2x))
C   calculate the initial conditions for the averaging
    nc=1
    nco=1
    NC2=1
    t0=0.
    areaf=0.
    tauf=0.
    tauno=0.
    areano=0.
    atauf=0.
    atauno=0.
    do 600 i=1,ls
        if(dsprnm(i).eq.'H2 ')ih2=i
        if(dsprnm(i).eq.'H2O ')iih2o=i
        if(dsprnm(i).eq.'NO ')ino=i
        if(dsprnm(i).eq.'O2 ')io2=i
    600 continue
C
C STEP 1 INTEGRATION
C
C   set initial fuel concentration CH2MI
    CH2MI=SNGL(PRC(ih2))
427 continue
    cnox=sngl(prc(ino))
    cfuel=(prc(ih2))
    CH2OM=CH2MI-CFUEL
    if(ch2om.gt.1.d-20.and.nco.gt.8)goto 504
    IF(NCO/50*50.EQ.NCO)write(10,423)nco,P,T,phi,cfuel,h2os1
    1timil
423 format(i4,f5.1,f8.1,1p,8e10.3)
C   calculate the initial conditions for the averaging
    if(nc.lt.2)goto 1500
    if(timil.gt.1.)goto 1500
    if(nc.eq.1)tstart=timil
    if(nc.eq.1)t0=timil
    if(nc.eq.1)tafo=-(prc(ih2)/W(ih2))*1.d3
C   if(nco.eq.2)edd=15.*tafo
    if(tn.eq.t0)goto 424
    if(W(ih2).ne.0.)tauf=-(prc(ih2)/W(ih2))*1.d3
    if(nc.eq.q)atauf=tauf
    if(tauf.le.0.)goto 899
    nco=nco+1
    areaf=areaf+(1./tafo+1./tauf)/2.*dble(tn-t0)
    timet=timil-tstart
    atauf=dble(timet)/areaf

```



```

        if(nco/1*1.eq.nco)write(11,423)nc,P,T,phi,cfuel,O2,tauf,atauf,
        ltimil
        taufo=tauf
        xrate=(w(ino))
424 if(nco.eq.1)tauni=(1.D0/(xrate))*1.e3
        tauno=sngl(1.D0/(xrate))*1.e3
        if(t0.eq.tn)goto 339
        if(tauno.lt.0.)go to 339
        areano=areano+(1./tauno+1./tauni)/2.*dble(tn-t0)
        atauno=dble(timet)/areano
        tauni=tauno
c      if((nc/10*10).eq.nc)write(13,501)nc,P,T,cnox,tauno,
c      latauno,eratio,timil
339 continue
338 format(i7,1e12.3,7e12.4)
        t0=tn
504 continue
431 format (f12.2,3e13.5,f8.3,f8.3,e13.5)
C do step 2 calculations
        IF(CH2OM.LT.1.d-20)GOTO 899
        if(W(ih2).ne.0.)tauf=-(prc(ih2)/W(ih2))*1.d3
        xrate=(w(ino))
        tauni=(1.D0/(xrate))*1.d3
        pl=dlog(p)
        tol=1./T
        cfuel=(prc(ih2))
        h2o=sngl(prc(iih2o))
        h2osl=sngl(dlog(prc(iih2o)))
        H2OML=dLOG(CH2OM)
        fo=dlog(cfuel)
        if(W(ih2).ne.0.)tauf=-(prc(ih2)/W(ih2))*1.d3
        if(tauf.le.0.)goto 899
        tal=dlog(tauf)
        if(tauni.gt.0.)taln=dlog(tauni)
        NC2=NC2+1
        if(nc2/100*100.ne.nc2)goto 899
c      if(tauf.gt.5..or.tauf.lt.1.e-6)goto 899
        if(timil.gt.1.)next=.true.
        if(timil.gt.1.)goto 1500
        write(10,423)nc2,P,T,phi,cfuel,h2o,ch2om
        1,tauf,timil
        write(26,447)timil,prc(5),prc(2),prc(1),prc(4),prc(3),prc(6),
        lprc(10)
447 format(1p,9e13.4)
        write(27,900)NC2,timil,philn,pl,tol,fo,h2oml,tal,tauf,ch2om
        write(28,900)NC2,timil,philn,pl,tol,fo,h2oml,taln,tauni
900 format(I5,1e10.3,1p,9e11.3)
        if (nc.gt.2)go to 502
        write(6,1602)ih2,iih2o
1602 format(' ih2 ',i5,' iih2o ',i5)
        coci=prc(ih2)/ch2mi
        if(coci.gt.0.)totau=-log(coci)
        write(6,1600)timil,tauf,atauf,h2ol,h2oml
1600 format(' timil ',e12.3,' tauf ',e12.3,' atauf ',e12.3,
        1' h2ol ',e12.3,' h2oml ',e12.3)
        write(6,1603)ch2mi,cfuel,ch2om

```

```

1603 format(' ch2mi ',e12.3,' cfuel ',e12.3,'ch2om ',e12.3)
      write(6,1601)coci,totau
1601 format(' h2/h2i ',e12.3,' timil/tau overall ',e12.3)
899 continue
501 format(i4,f7.4,f7.1,4e12.5,f6.3,f9.3)
1500 continue
      nc=nc+1
      if(nc.gt.3)goto 502
      DO 435 IJ=1,MAX
      IF (IJ.GT.LS.OR.IJ.GT.LR) GO TO 435
      TCON(IJ)=SNGL(PRC(IJ)/W(IJ))
      FMOL=SNGL(SIGMA(IJ)*MIXMW)
      WRITE (LWRITE,175) DSPNM(IJ),PRC(IJ),FMOL,W(IJ)
430  WRITE (LWRITE,185) IJ,RATE(IJ),PRX(IJ),EQUIL(IJ)
C430  continue
435  CONTINUE
502  IF (WELSTR) GO TO 446

```

## Appendix C

### Run Input for GLSENS

Run input for H2 for GLSENS TYPICAL FOR STEP ONE AND TWO

H2/AIR INPUT

CO2     AR

TIME     PRESSURE             H2

  &prob TCON=.TRUE.,CT0=0.5,

  IPRINT=1,end=1.e-4,&end

  &start time=0.,ERATIO=0.3,SCC=0.0,SCOX=0.,SCH=2.0,

  NOXRAT=3.76,ARAT=0.,CRAT=0.,T=1000.,&end

END

  &solver mxstep=20000,emax=1.e-15,atolsp=1.e-15,maxstp=190000,&end

INIT

ALLSP    END

SENSVAR

ALLSP    END

REAC

FINIS

H2O2 INPUT FOR H2/O2 STEP ONE AND TWO

TIME     PRESSURE             H2

  &prob TCON=.TRUE.,CT0=0.5,

  IPRINT=1,END=1.E-4,&END

  &start time=0.,ERATIO=0.1,SCC=0.0,SCOX=0.,SCH=2.0,

  NOXRAT=0.0,ARAT=0.,CRAT=0.,T=1000.,&end

END

  &solver mxstep=20000,emax=1.e-15,atolsp=1.e-15,maxstp=190000,&end

INIT

ALLSP    END

SENSVAR

ALLSP    END

REAC

FINIS



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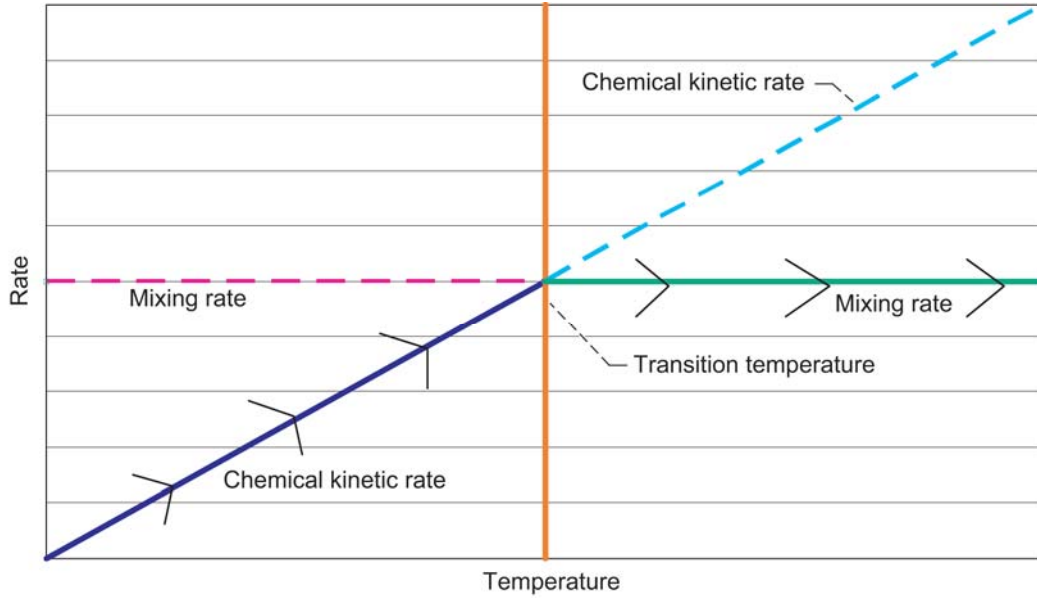


Figure 1.—Magnussen mixing model.

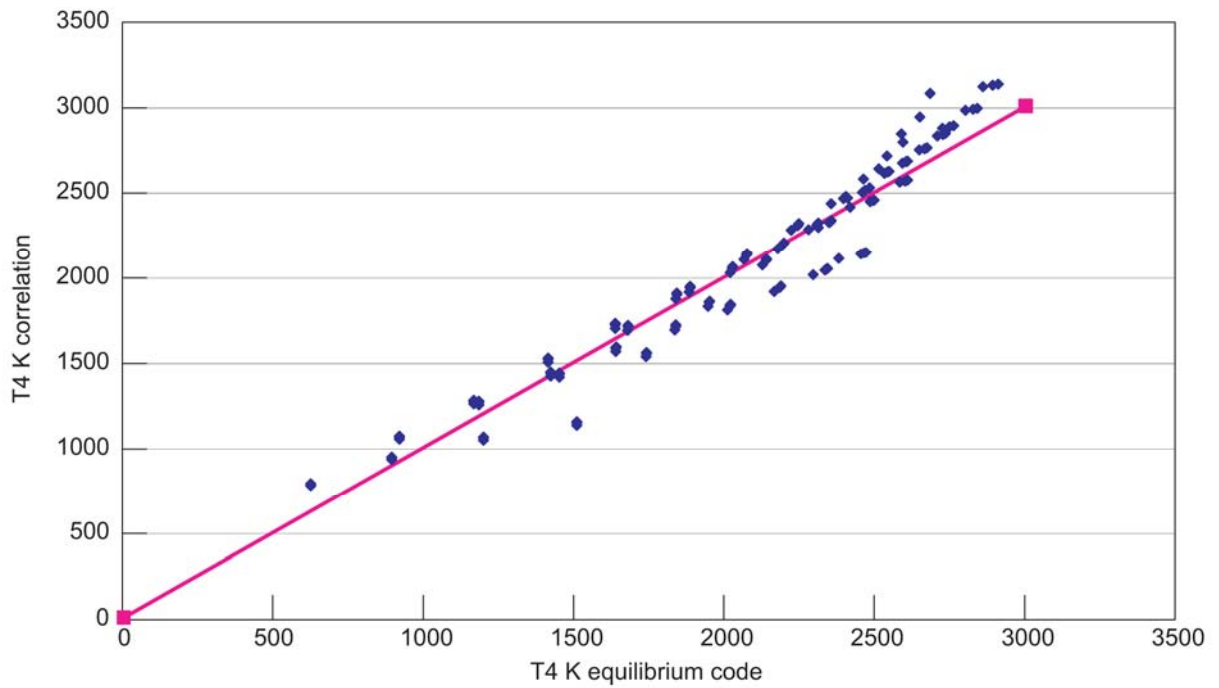


Figure 2.—H<sub>2</sub>/air T4 parity (lean)  $R^2 = 0.936$ .

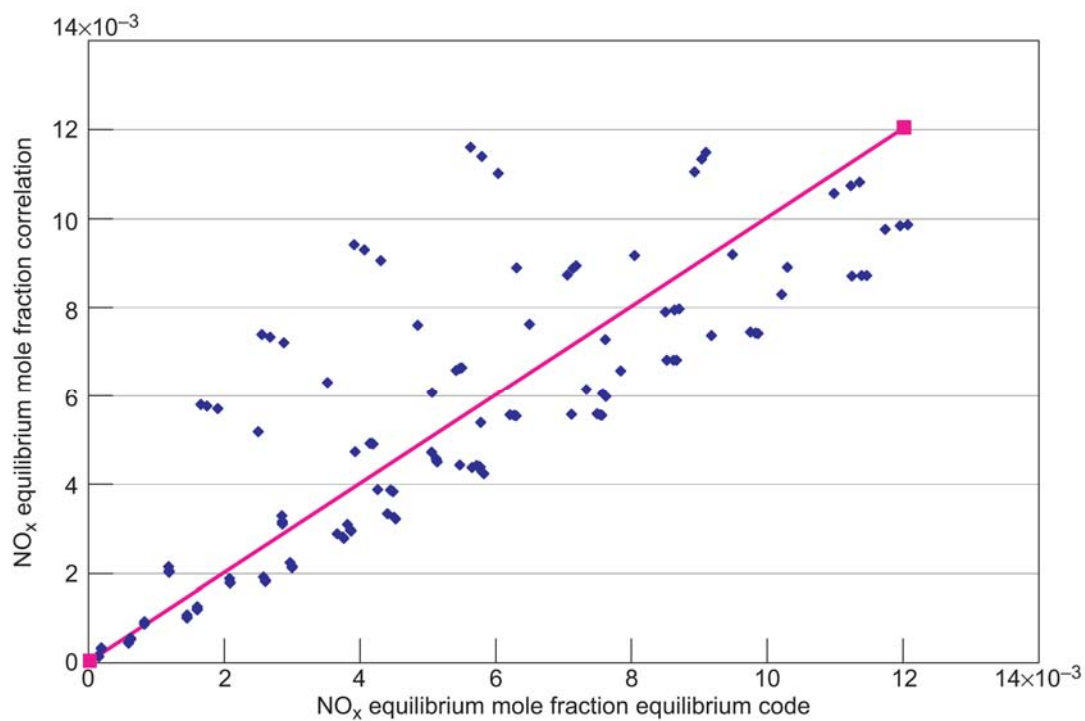


Figure 3.—NO<sub>x</sub> mole fraction equilibrium parity (lean)  $R^2 = 0.977$ .

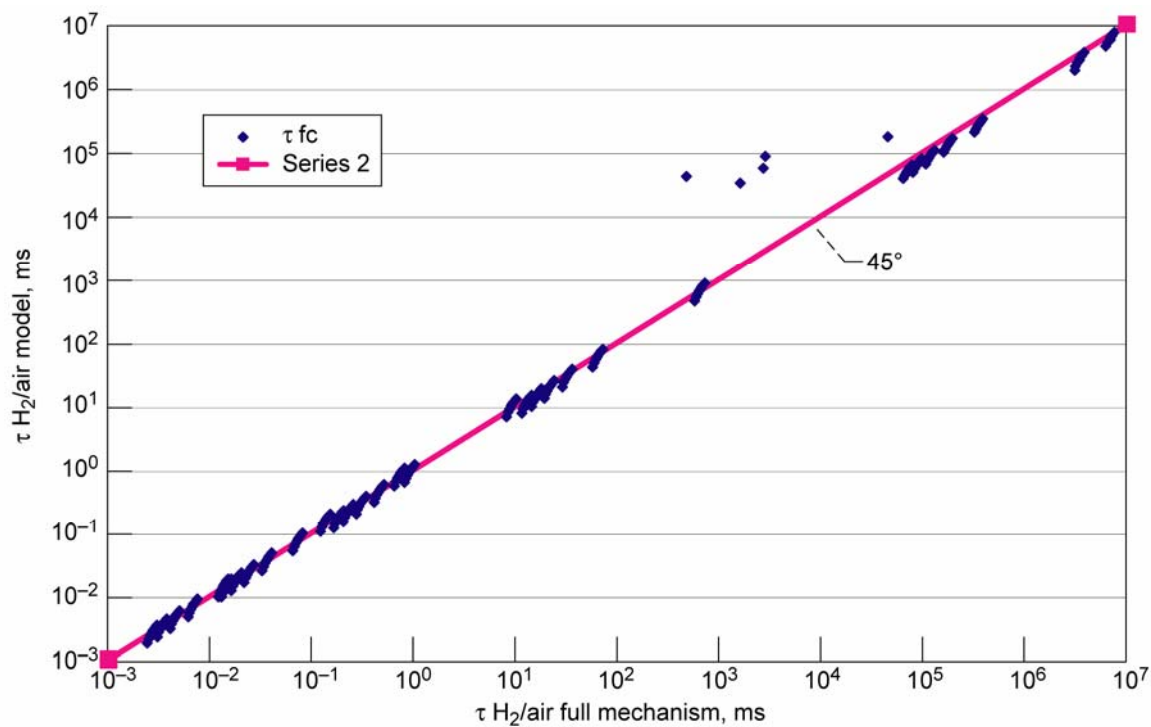


Figure 4.—Kinetic H<sub>2</sub>/air parity plot step one (lean)  $R^2 = 0.994$ .

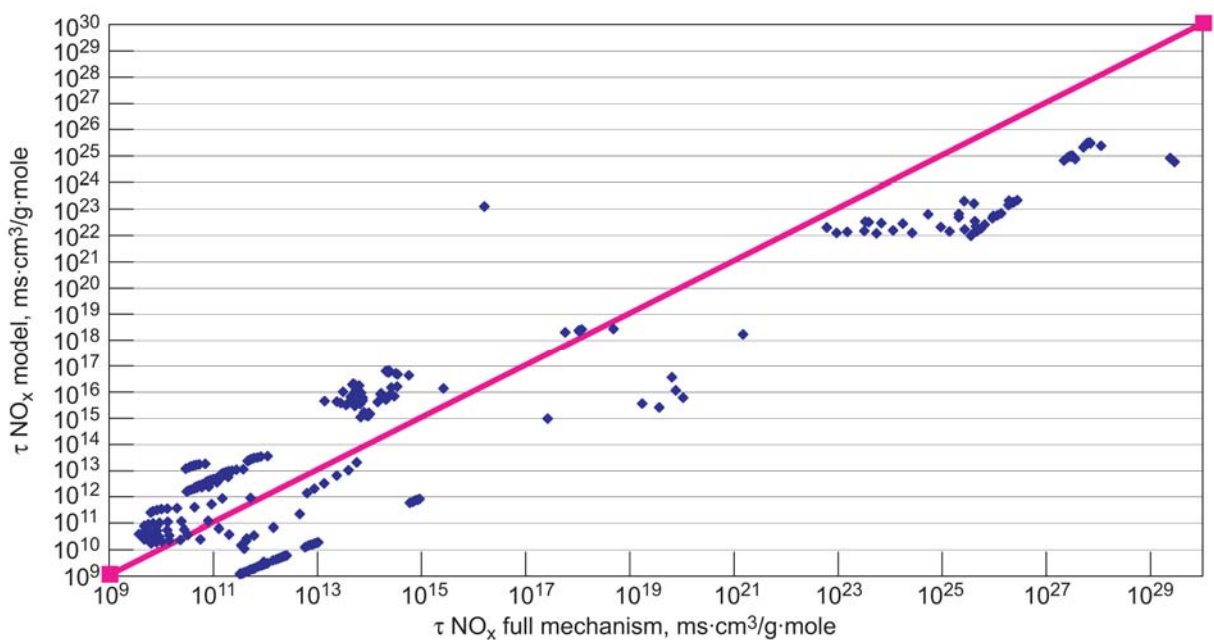


Figure 5.—Kinetic H<sub>2</sub>/air NO<sub>x</sub> parity plot step one (lean)  $R^2 = 0.647$ .

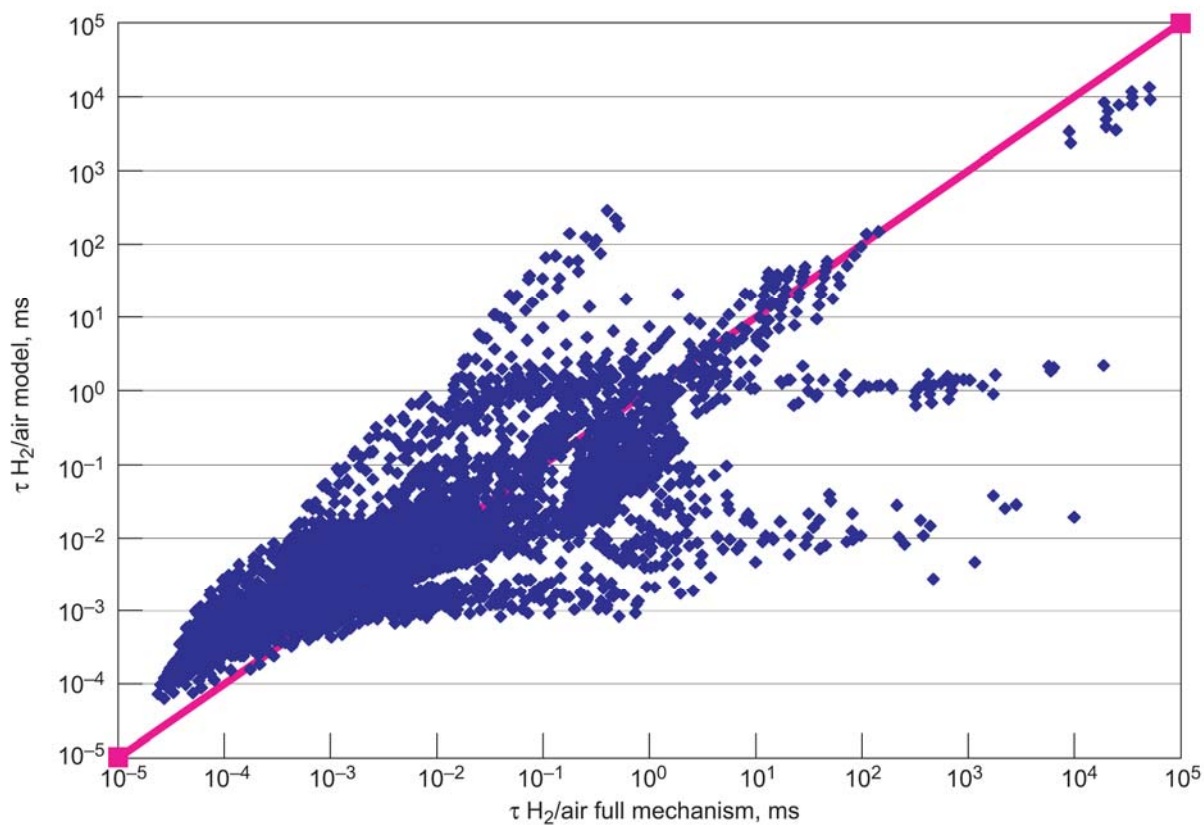


Figure 6.—Kinetic H<sub>2</sub>/air parity plot step two (lean)  $R^2 = 0.604$ .



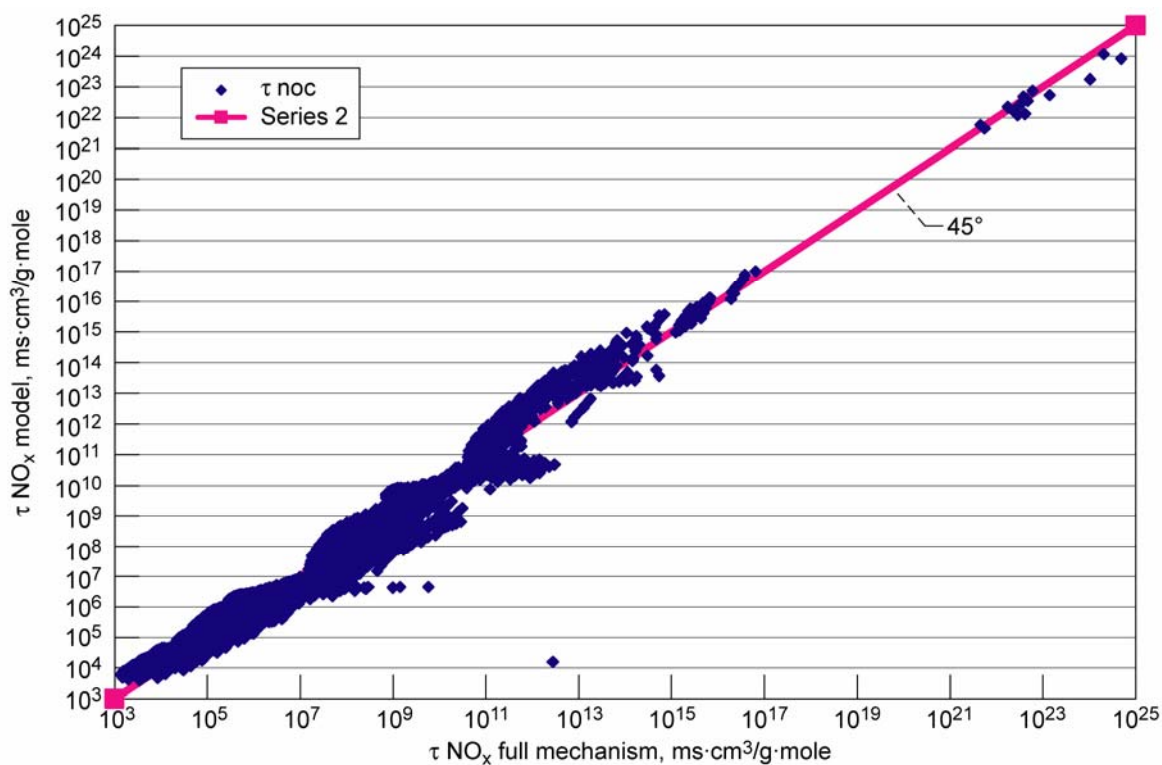


Figure 7.—Kinetic H<sub>2</sub>/air NO<sub>x</sub> parity plot step two (lean) R<sup>2</sup> = 0.976.

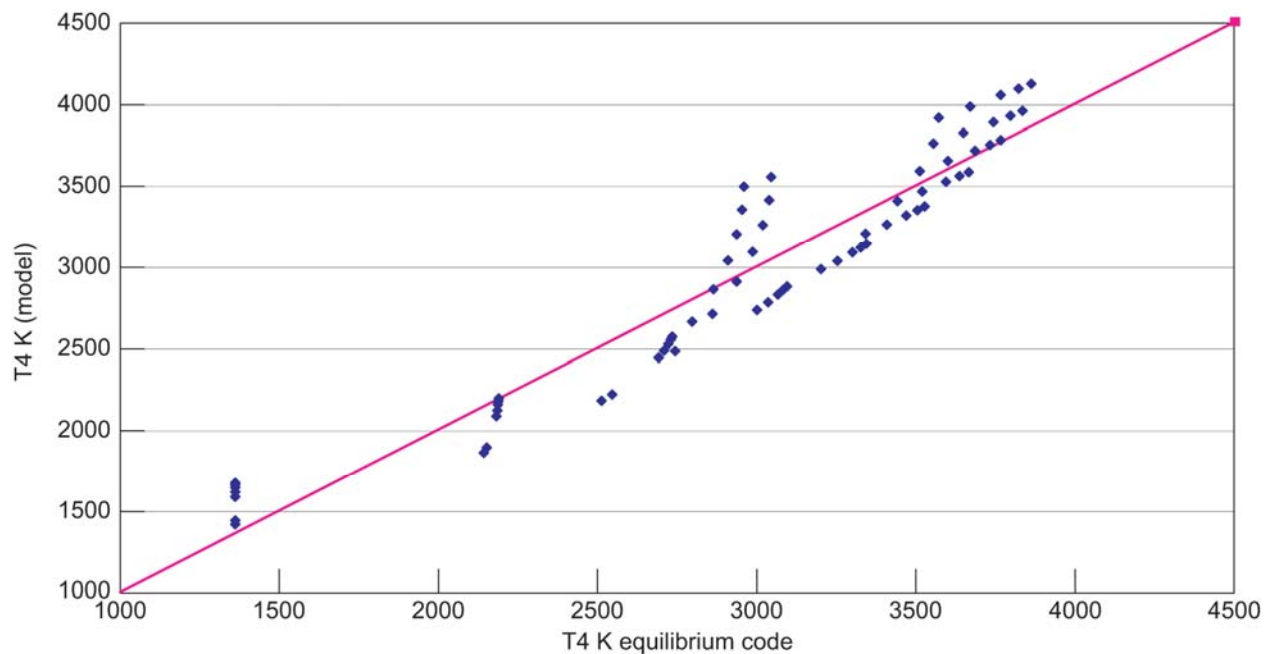


Figure 8.—Equilibrium H<sub>2</sub>/O<sub>2</sub> T4 parity plot (lean) R<sup>2</sup> = 0.91.

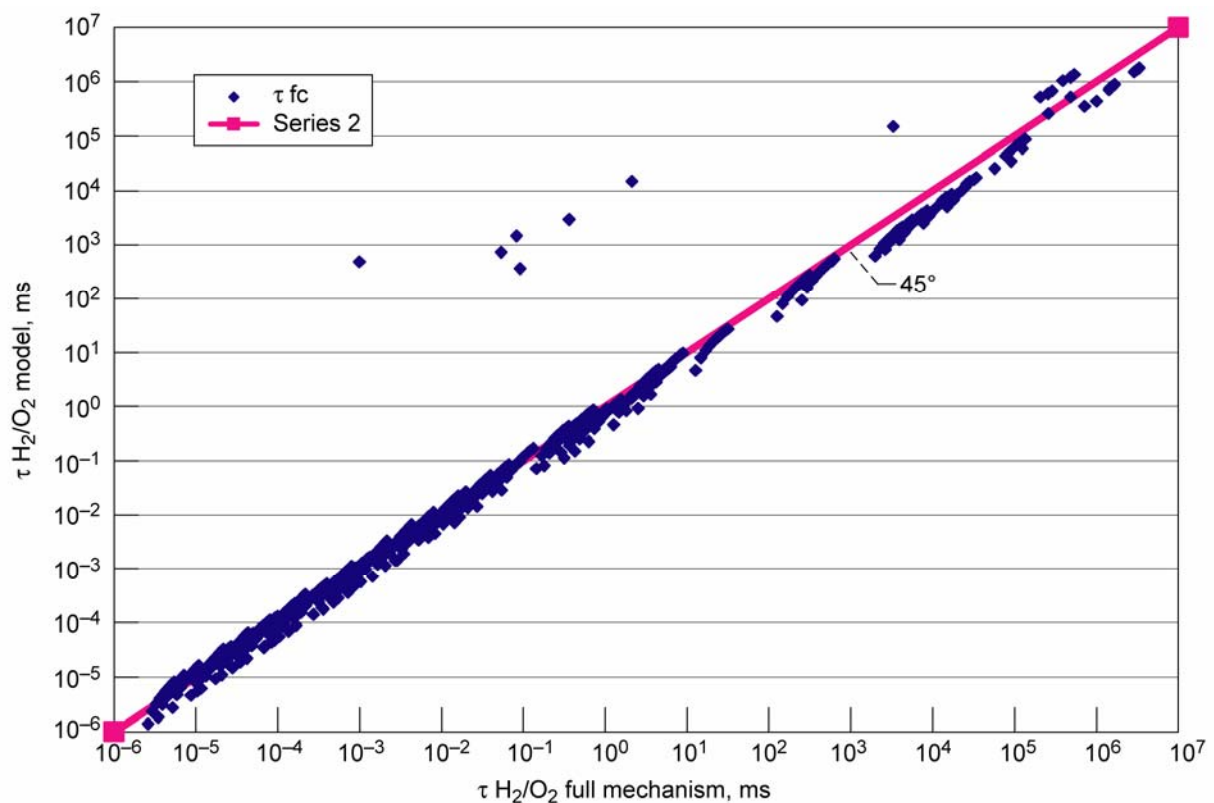


Figure 9.—Kinetic H<sub>2</sub>/O<sub>2</sub> parity plot step one (lean) R<sup>2</sup> = 0.956.

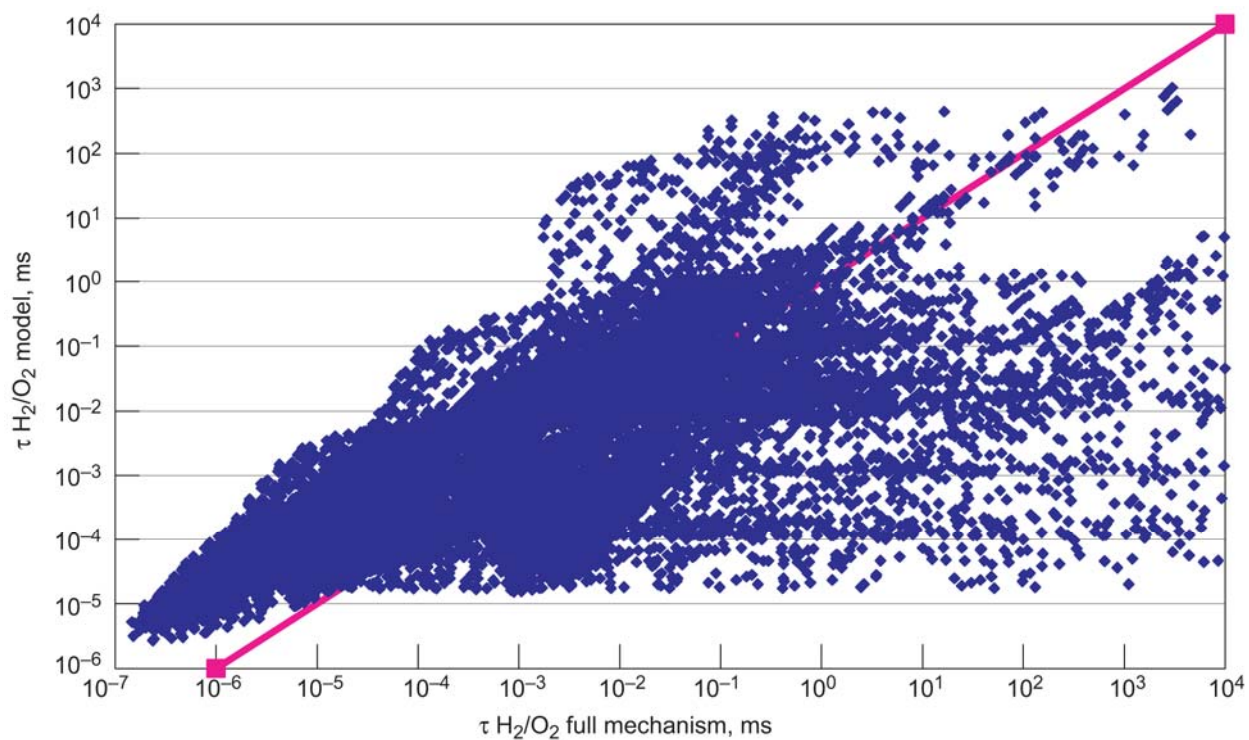


Figure 10.—Kinetic H<sub>2</sub>/O<sub>2</sub> parity plot step two (lean) R<sup>2</sup> = 0.494.

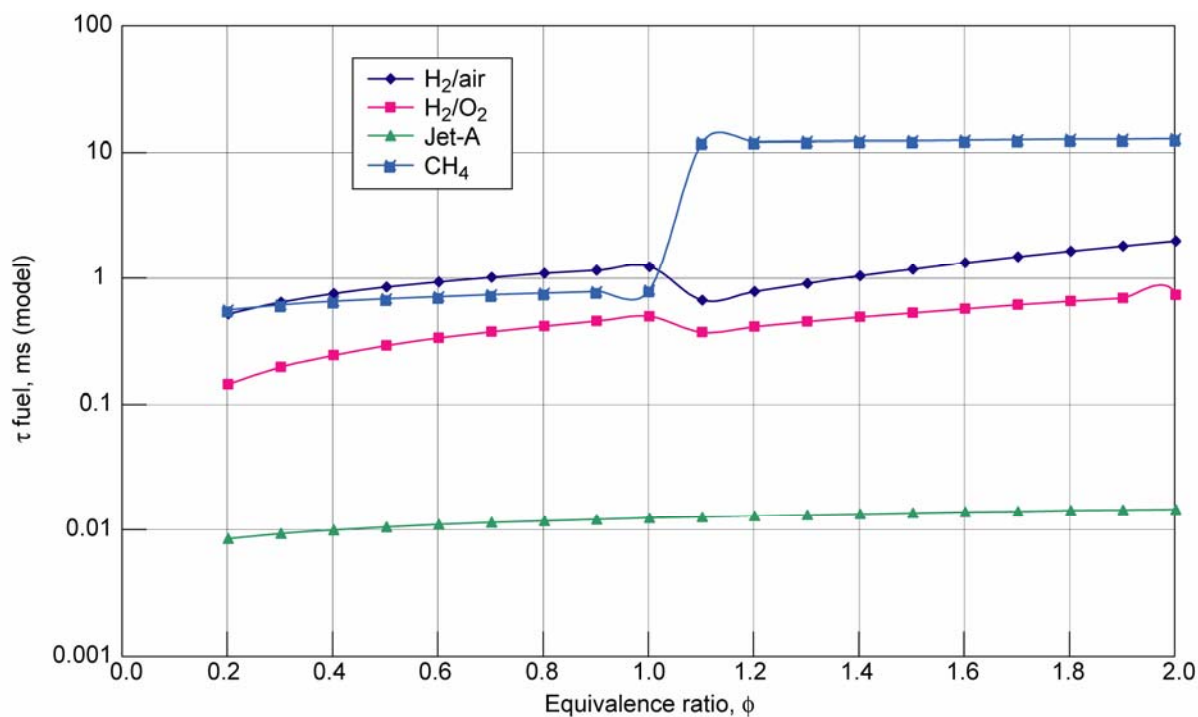


Figure 11.—Kinetic  $\tau_{\text{fuel}}$  at 10 atm and 2000 K for fuel reactions step one (lean and rich), time = 0.

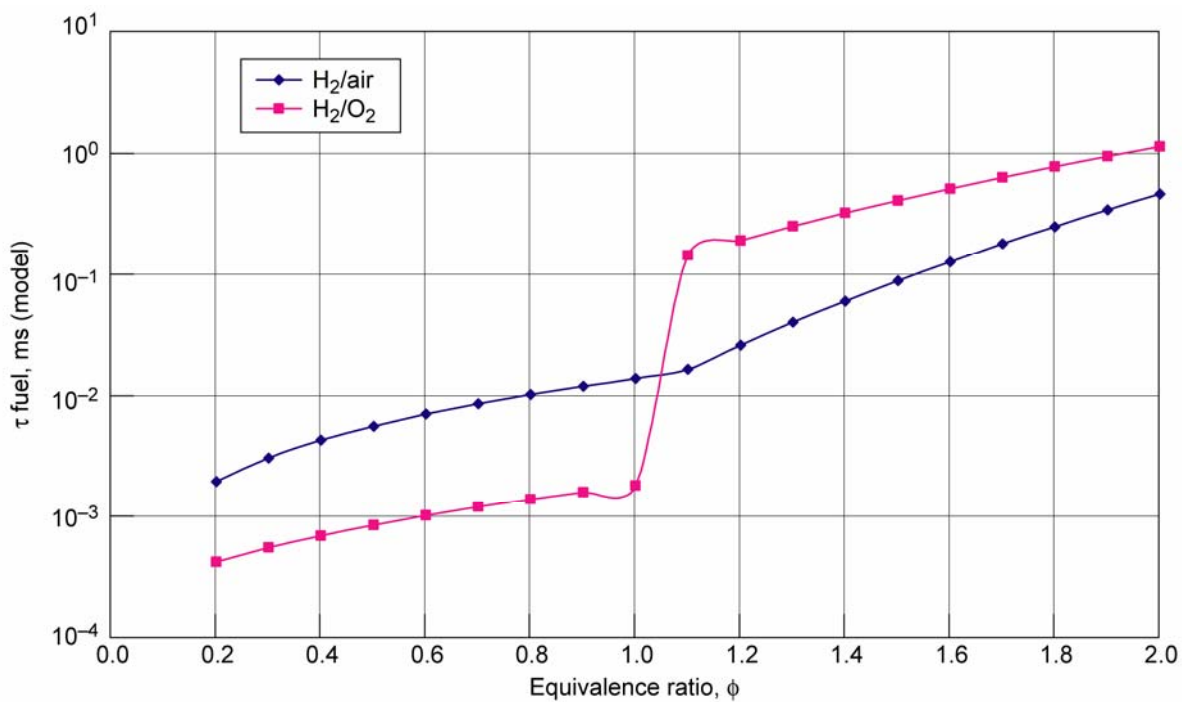


Figure 12.—Kinetic  $\tau_{\text{H}_2}$  at 10 atm and 2000 K step two (lean and rich), INEFF = 0.5.

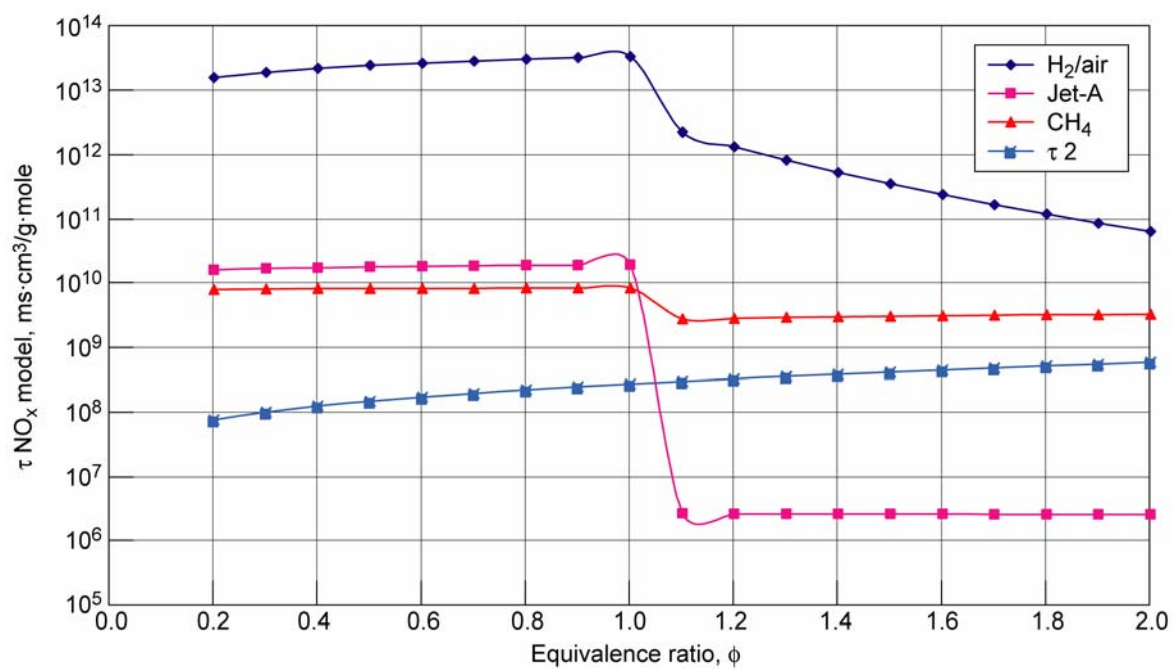


Figure 13.—Kinetic  $\tau_{NO_x}$  at 10 atm and 2000 K for  $NO_x$  reaction step one multiple fuels, time = 0,  $\tau_2$  for  $H_2/air$  (lean and rich), and INEFF = 0.5.

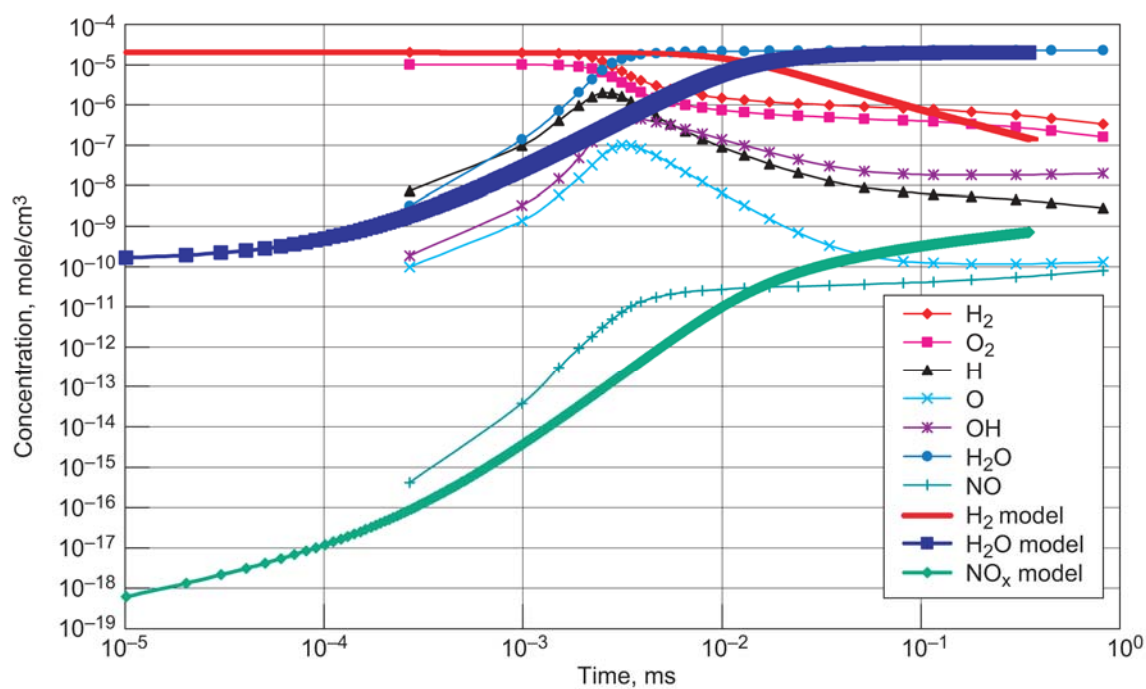


Figure 14.— $H_2/air$  concentration versus time, 2000 K, 10 atm,  $\phi_0 = 1$ .

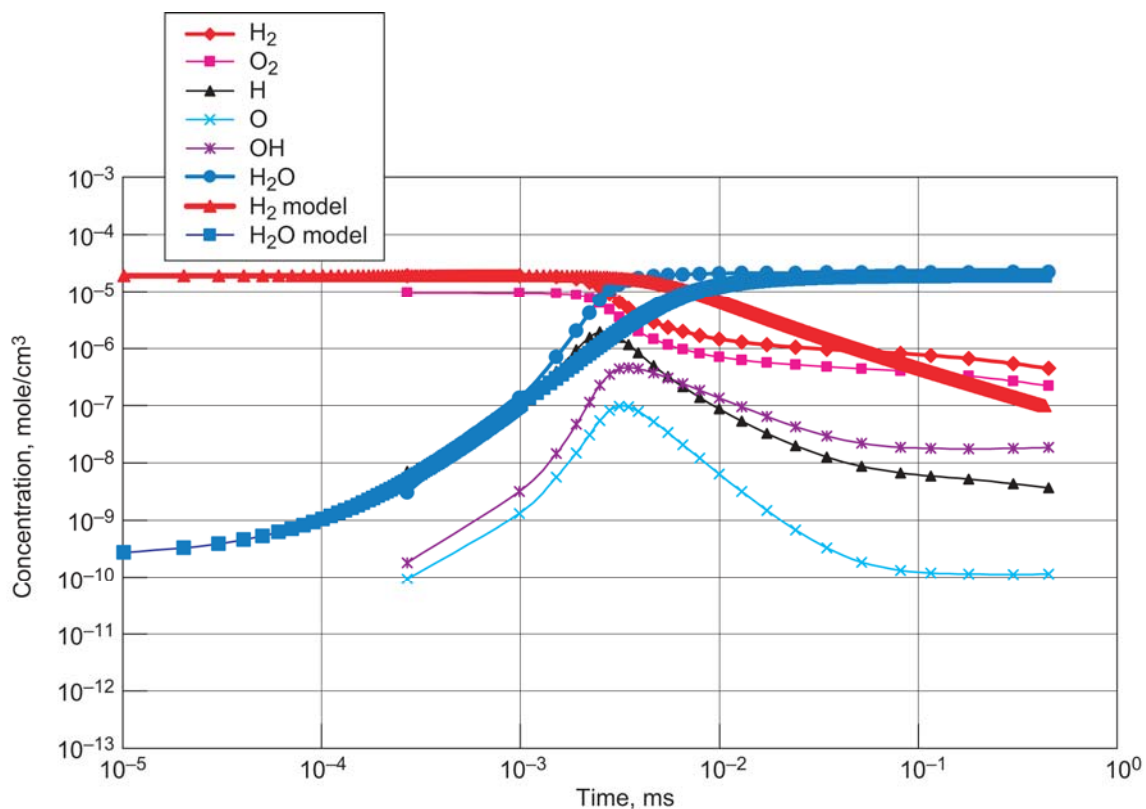


Figure 15.— $\text{H}_2/\text{O}_2$  concentration versus time, 2000 K, 10 atm,  $\phi_o = 1$ .

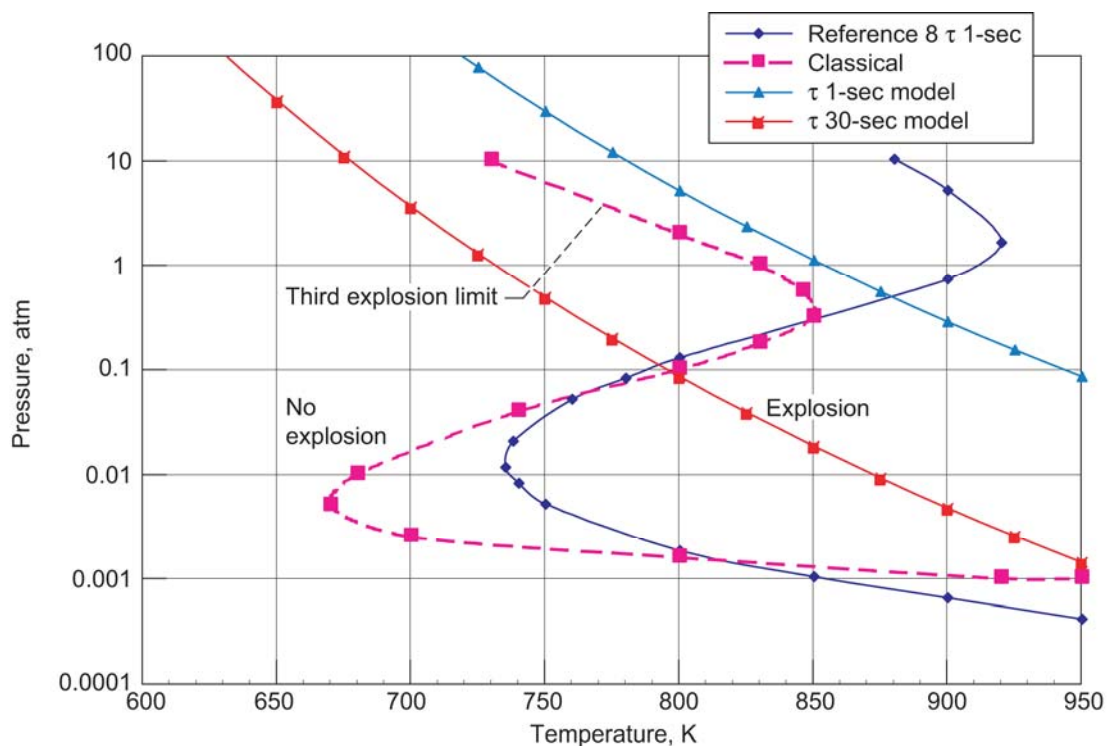


Figure 16.—Explosion limits for  $\text{H}_2$  at low pressure.

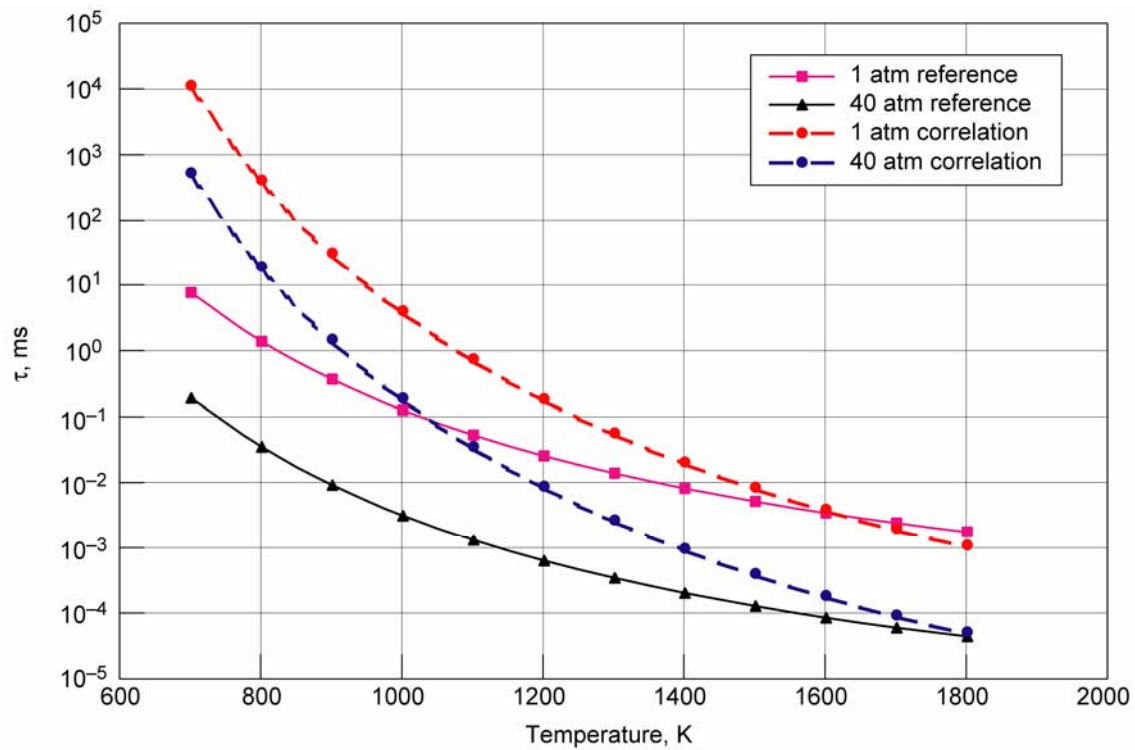


Figure 17.—Autoignition times of  $H_2$ , reference 9.



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